

Formation of Detonation Diamond Layers on Silicon by the Aerosol Method

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Abstract—An aerosol method for deposition of nanometer-thick layers of detonation diamonds has been developed. Application of a suspension of deagglomerated diamond particles onto substrates from an aerosol provides deposition of small-size drops, with the ultrasonic spraying of the suspension precluding formation of secondary agglomerates of nanodiamond particles in the course of sample drying. The layers are promising for high-precision studies of the structure and chemical composition of the surface of isolated nanodiamond particles.

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The steadily increasing interest in nanodiamonds is due to the wide prospects for their application in nanoelectronics and, especially, for solution of a wide variety of biological and medical problems [1, 2].

Ultradispersed diamonds produced by detonation synthesis (or detonation nanodiamonds, DNDs) are composed of a multitude of nanodiamond particles with an average size of 4.5 nm. The surface of each particle contains carbon in a state different from that in diamond (sp^3 -hybridized), in amounts from several atoms arranged in chains to several layers of sp^2 -hybridized carbon. Various oxygen- and hydrogen-containing functional groups are present on the surface, with their number and composition dependent on the technology of synthesis, purification, and further processing of DNDs. Because about 20% of carbon atoms constituting the DNDs belong to the surface, it is the surface that determines most of their properties and the possibility of their application as a promising functional nanomaterial [3].

To diagnose the chemical composition and the surface electronic structure of DND particles, it is necessary to employ surface-sensitive methods with an information depth not exceeding 1–2 nm. The methods of electron spectroscopy possess these properties. Using a synchrotron as a source of monochromatic radiation with tunable energy and ultrahigh intensity significantly extends the capacity of photoelectron spectroscopy (PES) by making it a very versatile tool for quantitative analysis of the electronic structure and chemical composition of any solid samples, including DNDs.

However, the pronounced dielectric properties of diamonds (real electrical resistivity exceeding $10^{13} \Omega \text{ cm}$) leads to an unpredictable shift of features in PES [4]. Similarly, static charging of samples studied by scan-

ning electron microscopy distorts the pattern of the surface morphology and changes the image contrast of a charged region, compared with that uncharged [5]. Therefore, the application of methods based on high-intensity electron or photon beams to studies of chargeable films inevitably necessitates use of special procedures for compensating for the static charging effect [5, 6].

Until recently, there has been an additional problem in studying the chemical composition and electronic structure of the surface of DND particles: it is difficult to obtain isolated nanodiamond particles. Similarly to most ultradispersed materials, DNDs can form agglomerates both in solution and when being dried. A distinctive feature of the DNDs is that high-density agglomerates that are difficult to destroy with sizes of 100 nm and more are formed during its synthesis [3]. The agglomerated DNDs cannot be fully purified to remove impurity phases, including sp^2 -hybridized carbon on the particle surface. In deposition of an agglomerated material on a substrate, the smallest thickness of a layer and its uniformity mostly depend on the size of the agglomerates. It is noteworthy, however, that sp^2 -hybridized carbon leads to weak charging under a photon beam of even micrometer-thick layers produced by the simple method of drop deposition from a DND solution [4].

After the deagglomeration problem was successfully solved, it became possible to obtain aqueous DND suspensions constituted by isolated nanodiamond particles with a size of 4.5 nm and a surface free of the sp^2 phase [3, 7]. The appearance of a material of this kind opens up prospects for high-accuracy studies of the structure and chemical composition of the surface of isolated nanodiamond particles. Application of scanning electron microscopy and photoelectron

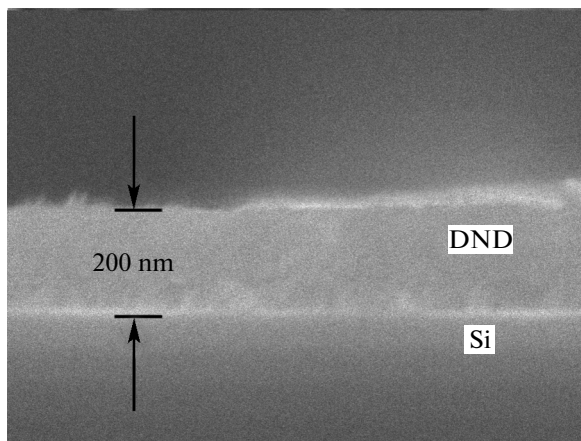


Fig. 1. Cross-sectional electron-microscopic image of a DND film formed on the surface of a silicon substrate by the aerosol method as a result of five “aerosol delivery–drying” cycles.

spectroscopy for studies of this kind necessitates development of methods for deposition of nanometer DND layers with uniform thickness and rather high conductivity. There is an additional requirement for PES samples that their stability should be preserved in prolonged high-vacuum annealing (in a vacuum with a residual pressure of $\sim 10^{-10}$ Torr at temperatures up to $T \sim 1000^\circ\text{C}$). The primary goal of the study reported here is to develop DND layers possessing the above properties.

In this study, we used DND powders annealed in air, from which DND suspensions in deionized water (resistivity $R > 10^6 \Omega \text{ cm}$) were prepared with a concentration of 0.1 wt %. For this purpose, weighed portions of the powders were placed in water and subjected to prolonged ultrasonic dispersion. The frequency of the ultrasonic generator was $F = 22 \text{ kHz}$ at sonic power $P = 600 \text{ W}$. The resulting suspensions were further processed by centrifugation to separate residual aggregates (with sizes of 80–100 nm) of DND particles. As a result, the suspensions obtained contained only free DND particles with a size of 4.5 nm [7].

Wafers of standard semiconductor silicon with a resistivity of $0.1 \Omega \text{ cm}$ used to fabricate semiconductor devices served as substrates. The substrates were separated by scribing into $7 \times 5\text{-mm}$ rectangular fragments, decreased by boiling in organic solvents, and treated with a mixture of NH_4OH and H_2O_2 . To form layers, a suspension of DND particles was applied to the upward-facing surface of horizontally arranged substrates. In the course of drying of the aqueous suspension, separate drops are inevitably formed on the silicon surface, with the area of these drops subsequently decreasing and the concentration of DND particles growing within these drops [8]. The larger the drops, the stronger the nonuniformity of the layer obtained upon drying a sample. This circumstance strongly hinders obtaining uniform DND layers on surfaces with

a nonzero wetting angle. Depositing a suspension of deagglomerated DNDs onto substrates from an aerosol created by ultrasonic spraying is a very promising way to solve this problem. The aerosol method provides deposition of small-size drops, and the ultrasonic treatment of the suspension additionally precludes formation of secondary DND agglomerates in drying of a sample.

An ultrasonic generator with a working frequency of 2.3 MHz, maximum power of 18 W, and a semi-spherical emitter was used in the aerosol source. The shape of the emitter made it possible to focus the energy into a point near the surface of the suspension filling the vessel in which the emitter is placed. When operating, the generator created a permanent flow of the aerosol, which contained spherical drops ($\sim 1 \mu\text{m}$ in size) of the aqueous DND suspension. To transport the thus-formed aerosol toward the substrate, air was delivered into the chamber with the aerosol at a flow rate of $50\text{--}100 \text{ cm}^3/\text{min}$. To make the suspension drying faster, the lower side of the substrate was heated with an 8 W IR lamp.

DND layers were deposited on the substrate surface in the mode of alternating periods of DND aerosol delivery and substrate drying. The durations of the former and the latter were 10–20 and 30–120 s, respectively. To form a layer with a thickness of 80–200 nm, three to five “aerosol delivery–drying” cycles were required. The state of the substrate surface during deposition of a suspension layer was monitored with an optical microscope.

The films were diagnosed at the Collective Use Center Materials Science and Diagnostics in Advanced Technologies at the Ioffe Physical-Technical Institute. The diagnostics included analyses of the surface morphology of the films by optical microscopy (Eclipse LV150 microscope, Nikon) and scanning electron microscopy (SEM) (JSM 7001F microscope, JEOL).

Figure 1 shows a cross-sectional SEM micrograph of a layer formed in five “aerosol delivery–drying” cycles with a thickness of about 200 nm. The surface roughness does not exceed 30 nm and is comparable with the variation of the layer thickness, which is well seen in the right-hand part of its surface image.

Figure 2a shows an optical micrograph of the surface of a sample covered with a nanodiamond layer with a thickness of 200 nm. It can be seen that no continuous layer is formed and the surface coverage and particle-size distribution are nonuniform. The SEM micrograph shows separate large (200–500 μm) and finer ($<100 \mu\text{m}$) drops. It is noteworthy that the patterns observed for freshly formed layers and for those subjected to a high-temperature annealing in a high vacuum do not differ in the surface coverage by DND drops. A slight change in the image contrast, associated with the static charging, was only observed in the region of the largest thickness of the deposited DND drops. It can be seen in the magnified SEM image of

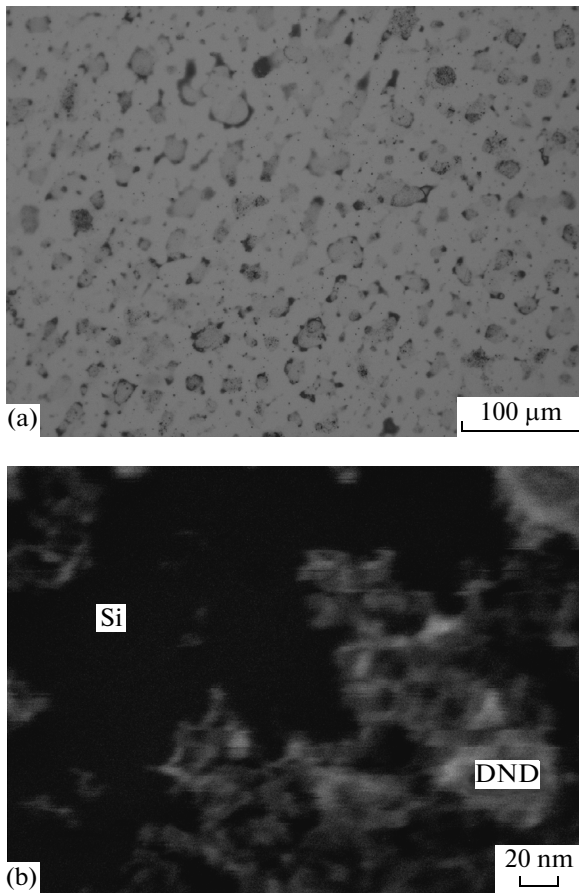


Fig. 2. Surface topography of a Si substrate covered with a 200-nm-thick DND layer (see Fig. 1) according to (a) optical microscopy and (b) SEM. The electron micrograph was obtained in the space between the drops forming the layer.

the sample surface between two drops (Fig. 2b) that the structure of a drop is rather loose, with the drop being composed of secondary aggregates of separate particles with a size of 10 nm. The absence of large dense agglomerates is confirmed by the cross-sectional micrograph in Fig. 1.

The photoelectron spectra of DND layers were obtained on an experimental station of the Russian–German channel of the BESSY-II electron storage ring (Berlin) [9] with a VG SPECS semispherical analyzer. Measurements were made with a monochromatized synchrotron radiation with photon energy $\hbar\omega = 700$ eV, which provided a simultaneous recording of photoelectrons corresponding to the core levels of silicon (Si2s, Si2p), carbon (C1s), and oxygen (O1s). Figure 3a shows a panoramic spectrum obtained from a sample with a 200-nm-thick layer (Figs. 1 and 2). The lines associated with the core silicon levels Si2s and Si2p, which have a doublet structure because of the partial oxidation of the silicon substrate, are present in the panoramic spectrum. This circumstance

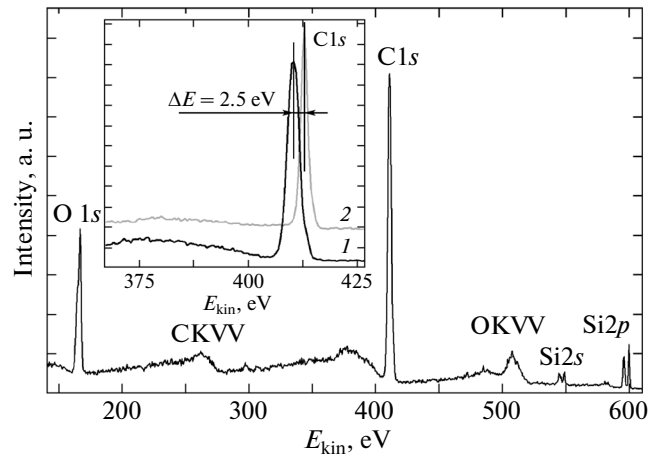


Fig. 3. Photoelectron spectrum of a 200-nm-thick DND film. The inset shows portions of the spectrum near the C1s line for (1) untreated and (2) annealed DND film. The measurements were made at photon energy $\hbar\omega = 700$ eV.

points to an island morphology of the DND layer under study.

The inset of Fig. 3 shows narrow portions of the spectra, which include only the C1s lines. Spectrum 1 in the inset corresponds to the untreated sample, and spectrum 2 corresponds to the same sample after high-temperature annealing at $T = 700^\circ\text{C}$ for 1 h. The close intensities of the C1s lines before and after the annealing of a sample indicate that the layers are stable against thermal treatments under high-vacuum annealing conditions. It can be seen in Fig. 3 that the relative energy shift of spectra 1 and 2 is 2.4 eV. It is known that high-vacuum annealing at $T = 700^\circ\text{C}$ causes a surface graphitization of DNDs [4, 10], which leads to a substantial increase in the conductivity of nanodiamond films and, consequently, nearly completely rules out the possibility of their static charging. Therefore, it can be assumed that the observed shift of spectrum 1 relative to spectrum 2 is due to the electrostatic charging of the untreated sample (spectrum 1). It is noteworthy that a similar shift of the photoelectron spectra for a micrometer-thick solid layer obtained upon drying of a drop of a deagglomerated DND suspension deposited on the substrate surface may reach values of about 6 eV and more; i.e., the island morphology noticeably accelerates the leakage of charge from the DND layer into the substrate.

Thus, it was shown that using the aerosol deposition method makes it possible to form nanometer DND layers with uniform thickness on silicon substrates. The aerosol method for application of deagglomerated DNDs provides deposition of small-size drops, and, in addition, the ultrasonic treatment of the suspension precludes formation of secondary DND agglomerates in drying of a sample. The island type of drop arrangement on the sample surface provides rather effective leakage of the static charge even

in the case of a nonconducting material, which diamond is.

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